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Advanced Geopolymerization Technology

Sudhir Sitaram Amritphale, Pooja Bhardwaj and Rainy Gupta

Abstract

Advanced geopolymerization is a novel approach for the manufacture of geopolymers via innovative solid-state chemistry mechanism in which tailored geopolymeric precursors in solid powder form are the one part requirement, and only water is needed for its conversion to advanced geopolymeric material, in contrast to conventional process, where first solution of alkali is prepared and then mixed with silicoaluminous source materials. This novel process comprises of tailored geopolymeric precursors in solid powder form which is obtained via mechanochemical dry grinding of raw materials for prolonged hours. The basic raw materials include vitreous silica- and alumina-containing waste material/by-products, e.g. fly ash, activated by sodium hydroxide with or without sodium silicate. The solid powder needs only addition of water to form geopolymeric material. The advanced process includes solid-state reactions during dry grinding process and enables sequencing of reactions for preparation of geopolymeric material.

Keywords: advanced geopolymers, mechanochemical grinding, fly ash, mechanism, solid-state

1. Introduction

Nowadays, safe disposal of different waste materials and industrial by-products is a key concern for global communities. In this context, the possibility to reuse industrial waste like fly ash to produce economical value-added important products, viz. geopolymers, by mitigating environmental hazards related to waste disposal is being explored on a large scale worldwide. The construction industries benefited using the concept of utilization of waste materials as resource material for the development of value-added materials certainly due to increasing cost and shortage of virgin raw materials. Reuse of industrial by-products to generate value-added products is one of the promising ways to attain green and sustainable development. Geopolymers are one of the commercially important products suitable for construction sector manufactured using waste products like fly ash, slag, etc.

In this work a brief status of barriers in adopting conventional geopolymerization and the challenges that must be overcome to commercialize geopolymers is considered as research objective and successfully achieved by introducing advanced geopolymerization process for the manufacture of solid-state advanced geopolymeric materials. The authors of this research focused their aim to establish a new chemical mechanism behind advanced geopolymerization contrasting reaction mechanism of conventional geopolymerization with an objective to broaden application spectrum of geopolymer which will be an important part of sustainable development.

2. Geopolymers

Geopolymers can be defined as covalently bonded noncrystalline Si—O—Al networks in which SiO₄ and AlO₄ tetrahedral frameworks are linked by shared oxygen to form a dense amorphous to semicrystalline three-dimensional framework. These are termed as geological polymers for the reason that their starting raw materials is of geological origin, and formation of geopolymer proceeds via inorganic polymerization and condensation reactions [1].

Prof. J. Davidovits in 1978 introduced the term geopolymer and described it as cement-free green cementitious material. These are the inorganic polymers obtained from alkali activation of aluminosilicate materials like fly ash. These are structurally and chemically comparable to natural rocks and are synthesized by the condensation mechanism similar to thermosetting organic polymers therefore termed as geopolymers. Earlier these were considered as a special case of 'soil cement/silicates' or alkali-activated aluminosilicate cement and termed as 'geocements' as it consists of three-dimensional framework of cross-linked polysialate chains [2, 3].

Geopolymers have the potential to replace ordinary Portland cement (OPC) and to overcome the limitations associated with OPC. The production of OPC requires high temperature for calcinations which is not a requisite for the production of geopolymers. Unlike OPC, the production mechanism of geopolymers does not produce greenhouse gas CO₂ and possess extraordinary chemical properties and mechanical strength. Thus, geopolymers are environment-friendly substitutes for OPC and are frequently referred to as 'green cement'.

Geopolymers can be produced from sources of geological origin (e.g. kaolinite, clay) or industrial by-products such as fly ash, granulated blast furnace slag, red mud, waste paper sludge, rice husk ash, wheat straw ash, etc. [4, 5]. The choice of source material in geopolymers technology depends upon the competitive cost, availability, and specific application. Fly ash [Class F fly ash]-based geopolymers is getting intense research interest in past few years. It is a coal combustion residue generated from thermal power plants extensively rich in silica and alumina content [6]. Alkali activation of reactive silica- and alumina-rich raw materials produces an intense 3D—Si—O—Al—O—polymerization network [7]. The compact 3D framework thus formed after hardening is known as geopolymer, and the complete process is termed as geopolymers (Figure 1).

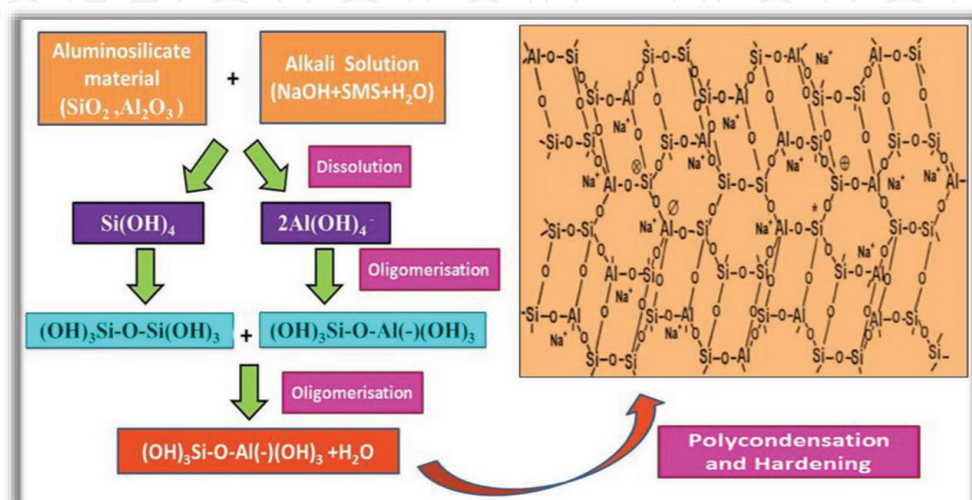


Figure 1.
Schematic representation of conventional geopolymerization.

3. Geopolymerization

Geopolymerization is the process of transforming aluminosilicate raw material into covalently bonded 3D network consisting $[\text{—Si—O—Al—O—}]_n$ bonds. In other words, geopolymerization process refers to geosynthesis, i.e. synthesis of chemically integrated minerals. The geopolymerization reaction results in the formation of viscous cementitious slurry which upon hardening forms strong, durable, and compact geopolymeric material [6, 8, 9]. Moreover much has been known about geopolymers and their chemistry in the last two decades, and efforts are still going on to uncover and discover some new scientific aspects of these wonder materials including some innovative applications besides construction sector [10, 11]. Considering this numerous scientists and researchers are engaged all over the world to extract out more potentiality in geopolymeric materials. The knowledge regarding geopolymer science during the last two decades indicated that the inorganic geopolymers are prepared by using starting raw materials which should essentially contain reactive silica and alumina in their structure, e.g. fly ash, and the alkaline activator solution containing mixture of sodium hydroxide and sodium silicate [12–14]. Conveniently we termed this process of developing geopolymer as conventional geopolymerization technology. It is to note that geopolymers can be prepared by utilization of different aluminosilicate sources such as red mud, blast furnace slag, kaolinite, rice husk ash, etc., and the starting material plays important role in deciding physicochemical and mechanical properties of geopolymeric material [15, 16]. The basic understanding of geopolymer formation and chemical reactions involved during conventional geopolymerization can be summarized as follows:

- Chemically, the conventional process includes solution chemistry mechanism in which amorphous aluminosilicate, e.g. fly ash, reacts with the solution of sodium hydroxide with sodium silicate and forms geopolymeric gel. Therefore geopolymer formation follows the bimolecular nucleophilic substitution (SN_2) mechanism [17]. Though geopolymerization reactions via solution chemistry mechanism cannot be fully understood, the complete mechanism can be understood under following heads including association, dissociation, oligomerization, and autopolycondensation.
- Step I is association, that is, association of water molecules to siloxane bond (—Si—O—Si—) present in aluminosilicate raw material. This association leads to the formation of an intermediate silicon species. The structure of intermediate silicon species is pentavalent making it highly reactive. The intermediate pentavalent silicon possesses distorted trigonal bipyramid structure and due to highly reactive nature undergoes dissociation rapidly to form silanols [12, 18–20].
- Step II is dissociation; in this step of SN_2 mechanism, intermediate pentavalent silicon undergoes dissociation in a concerted manner and forms silanol ($>\text{Si—OH}$) and aluminol ($>\text{Al—OH}$) groups [12, 18–22].
- The silanols further reacts and forms silanediol $\text{SiO}(\text{OH})_2$, silanetriol $\text{SiO}(\text{OH})_3$ and silanetetraol $\text{Si}(\text{OH})_4$ species. It is to be noted that the hydrated silica behaves as an acidic oxide in the presence of alkaline solution and possesses tendency to go into solution. Further, OH^- ions break siloxane bridges and result into the formation of alkaline silicates [23–26].

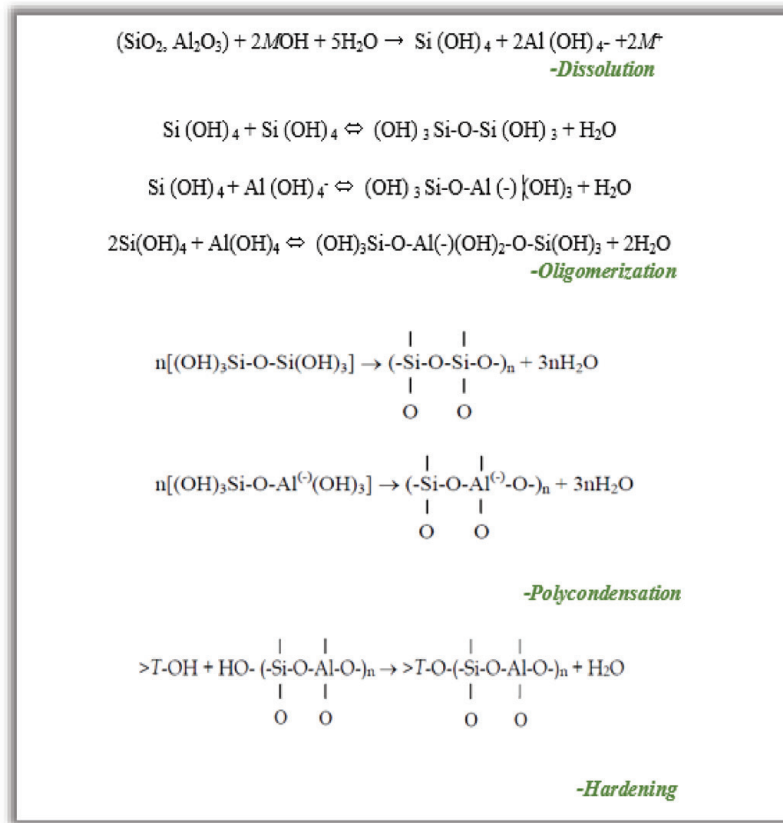


Figure 2.
Geopolymerization reactions proposed by [1–3].

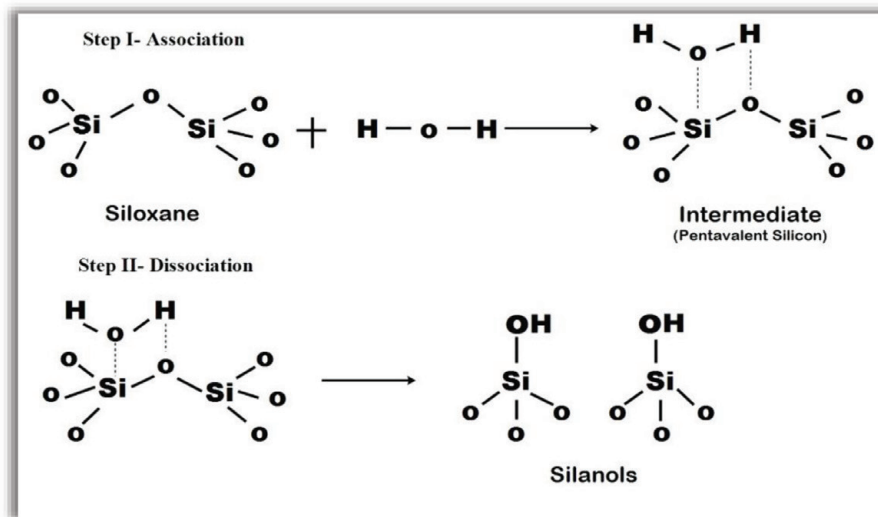


Figure 3.
Illustration of silanol and aluminol linkages in geopolymerization via SN_2 -solution chemistry mechanism.

- Similarly in aluminosilicate materials, oxides of Al get hydrated and form aluminol ($>\text{Al}-\text{OH}$) containing one negative charge and represented as $\text{Al}(\text{OH})_4^-$. Al^{3+} developed in fourfold coordination structure as it contributed only three electrons to bonding framework in place of four silicon atoms and because of this carry one negative charge [13].
- Autopolycondensation of silanols and aluminols takes place, and oligomers are transformed into polymer with the release of water molecules, further hardened to compact, strong 3D structure of $[-\text{Si}-\text{O}-\text{Al}-\text{O}-]_n$ framework.

In the geopolymeric chemistry, the negative charge on Al is balanced by cationic species like Na^+ to maintain the electrical neutrality. These are stereo-specific reactions which proceed with inversion of configuration. The rate of concerted mechanism depends on the concentration of both nucleophiles OH^- and the molecule undergoing attack. The complete reaction sequence for SN_2 mechanism is presented in **Figure 2**. On the other hand, **Figure 3** is the complete illustration of silanol and aluminol linkages in geopolymerization via SN_2 -solution chemistry mechanism.

4. Drawbacks of conventional geopolymerization process

In order to make large-scale commercialization of geopolymeric materials, it is essential to replace this conventional synthesis method because it is not a user-friendly process. The dissolution of NaOH in water is an exothermic reaction which leads to the formation of highly hazardous alkaline solution. The handling of alkaline solution is risky and prone to on-site hazardous accidents. Besides, the conventional method produced geopolymers with the properties suited for the confined commercial applications. With the conventional method, tailoring of properties of geopolymeric product is not possible. It is noteworthy that, for multifunctional applications of any product, tailoring of properties is highly desired for large-scale production. With this context, the conventional process seems to be ineffective regarding tailoring of properties for broad-range applications. Therefore to overcome these limitations, we introduce the concept of advanced geopolymerization and its basic reaction mechanism further in this chapter.

5. Advanced geopolymers

Advanced geopolymerization is a novel approach for the manufacture of geopolymers via innovative solid-state chemistry mechanism invented and patented by [27]. The advanced process is one part system, i.e. the tailored geopolymeric precursors in solid powder form are the one part requirement and only water is needed for its conversion to advanced geopolymeric material, in contrast to conventional process, where the first solution of alkali is prepared and then mixed with source materials. In the novel process, tailored geopolymeric precursors in solid powder form are obtained via mechanochemical dry grinding of raw materials for 8 hours. The basic raw materials include vitreous silica- and alumina-containing waste material, i.e. fly ash and NaOH with or without sodium silicate. This solid powder needs only the addition of water to form geopolymeric material. The advanced process comprises solid-state reactions during dry grinding process and enables tailoring of raw materials and sequencing of reactions among them for the preparation of geopolymeric materials. These geopolymeric materials can be used on site easily just like ordinary Portland cement.

6. Mechanochemistry/solid-state method

Grinding is an important operation that is used industrially for particle size reduction and production of large surface areas or liberating valuable things from any mineral. It comprises of different steps including material transport to grinding zone, grinding action, initiation and propagation of cracks, breakage of particle, or initiation of solid-state reactions within. Size reduction and intergranular breakage are significantly achieved by subjecting particles to mechanical pressure for a prolonged period. Generally, the breakage and fracturing process during grinding involves

rupturing of chemical bonds in order to create several reactive sites. The reactive sites when created are highly prone to undergo change and form some new chemical bonds with some other additive if present in the same reaction mixture [28]. This concept forms the basis of mechanochemical grinding reactions in dry state.

Mechanochemistry involves transformations supported by mechanical force in the form of milling or grinding [29–31]. The reactions proceed with grinding or milling are cleaner and efficient in terms of solvent, chemicals, materials, etc. [29]. It is known that the **mechanical activation** of aluminosilicate material, e.g. fly ash, results in enhanced reactivity. This is due to the combined effects of particle size reduction and physiochemical changes induced during high-energy milling of fly ash particles [32]. The **mechanochemical activation** on the other hand involves breakage of existing bonds and formation of new chemical bonds during high-energy milling process in the presence of any chemical agent in dry environment along with particle size reduction and increased amorphization. Solid-state chemical transformation occurs during mechanochemical grinding process of raw materials used for the advanced geopolymerization process.

The basic study for advanced geopolymerization was conducted by [27] in which grinding of fly ash along with NaOH in a ball mill exposed to mechanochemical forces that trench the internal bonding of fly ash and NaOH due to friction and impact with tumbling balls for prolonged durations. The amorphous reactive Si/Al phase disperses uniformly throughout the grinding process and reacts with Na^+ ions to form three intermediate phases which are termed as **precursor phases** for advanced geopolymerization reaction. The solid powder obtained after mechanochemical grinding of fly ash and NaOH is therefore termed as **advanced geopolymeric precursors** [8, 9, 33, 34].

Figure 4 is the pictorial presentation of the advanced geopolymerization technology which clearly shows that by just addition of only water to the advanced geopolymeric precursor phases, gelation occurred, and this gel essentially contain N—A—S—H phase [sodium aluminium silicate hydrate-geopolymeric phase].

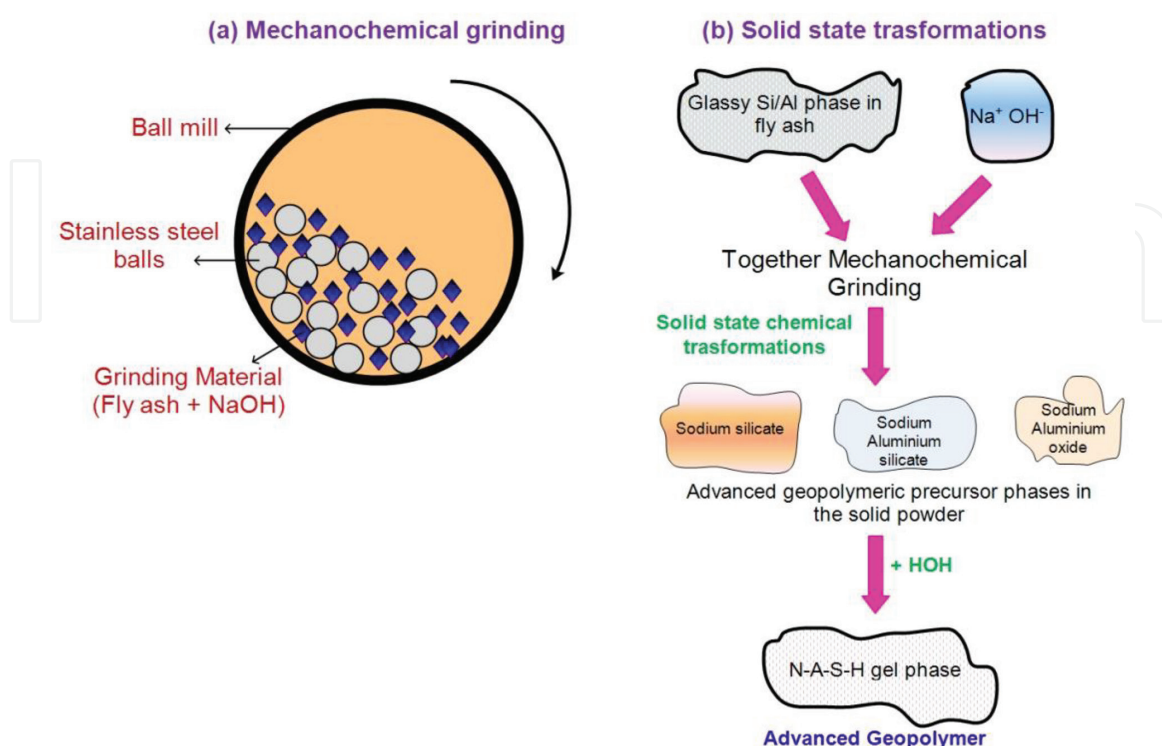


Figure 4. Mechanochemical grinding of raw materials and development of advanced geopolymeric precursor phases due to solid-state chemical transformations.

Later on, established by a number of experimental analyses, it can be said that advanced geopolymer possesses improved properties in terms of strength of the material and excellent corrosion protection [8, 9, 33–35].

7. Plausible solid-state mechanism for advanced geopolymerization

The solid-state mechanism involved in advanced geopolymerization reaction is different from that of conventional geopolymerization in the initial steps [33]. So the plausible chemical reaction mechanism for advanced geopolymerization can be understood under the following points:

- The 8 hours of mechanochemical activation of glassy silica/alumina in fly ash led to the dissociation of bonds present in glassy Si/Al phase; hence unlike conventional geopolymerization, the first step in the solid-state mechanism is **dissociation**. This step led to the formation of unstable silanone species —Si=O from siloxane —Si—O—Si— .
- This unstable Si=O is active in nature and rapidly transform into silanol even in the presence of minimum amount of water. So the next step is the association of intermediate with the water molecules to form silanol.
- First dissociation, followed by association reaction for the formation of advanced geopolymer, confirms its **unimolecular nucleophilic substitution** (SN_1) mechanism as also presented in **Figure 5**.
- In the presence of water, silanols form —Si—O—Al— linkages, and geopolymeric gel is then formed which on drying produces advanced geopolymeric material with considerable enhanced properties.

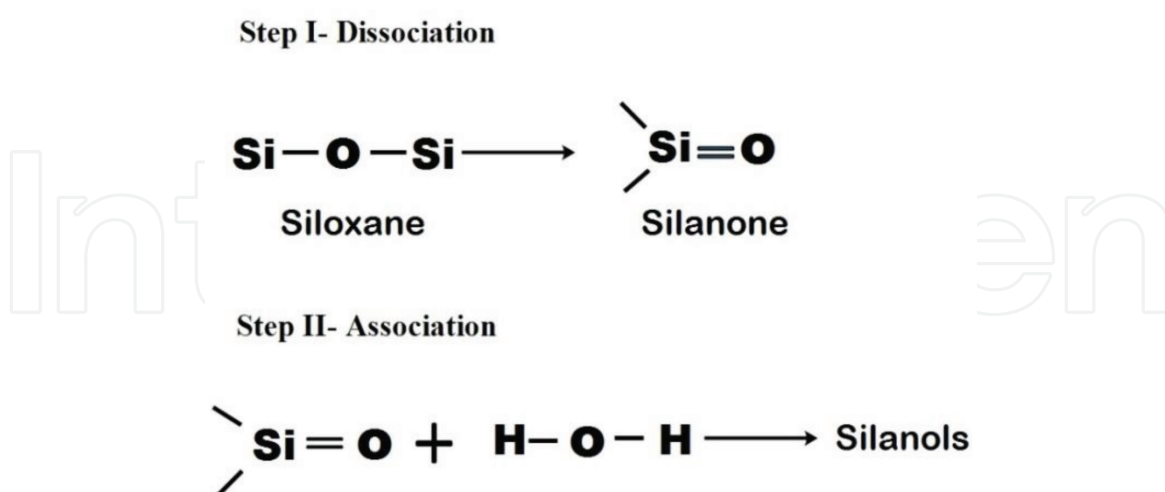


Figure 5.
 Illustration of formation of silanone and silanols for advanced geopolymerization via SN_1 solid-state chemistry mechanism [33].

8. Advantages of advanced process over conventional process

There are numerous advantages of advanced geopolymerization over conventional process. As we know, alkaline solution [pH around 10–14] is hazardous in nature which can cause skin hazards when accidentally comes in contact with people

dealing with it. The most important advantage of advanced geopolymerization is that it obviates the use of handling of highly alkaline solution as the advanced process involves reactions in dry state and only water is added to the geopolymeric precursor mixture which makes it a non-hazardous process. Unlike conventional geopolymerization, the geopolymeric precursor prepared by advanced process can be considered as ready-to-use premixture just like OPC which only requires addition of known amount of water to form cementitious material, thus facilitating its use for on-site application.

Moreover, advanced geopolymerization is advantageous in terms of its application spectrum. The advanced geopolymeric precursor material is suited not only for application as cementitious material but also best suited for prefabricated or pre-engineered geopolymeric end products which enhance its commercialization. Tailoring of properties can be performed at the precursor stage by altering basic formulations before the stage of mechanochemical grinding. In other words, to get the desired properties from geopolymeric end product, advanced geopolymerization technology allows the user to tailor properties of the geopolymeric end product which is not possible in the case of conventional geopolymerization. Also advanced geopolymers are capable to address the concerns related to high cost, transportation, and long-term storage that are important challenges for building and construction materials.

9. Advanced applications

Having all the properties required for traditional applications of geopolymers, the advanced geopolymers also offer additional commercial applications due to their eco-friendlier and user-friendlier approach. The advanced geopolymerization process via solid-state route enables the tailoring of the properties of end products as per requirement. Some of the important applications of advanced geopolymers are given below:

1. Advanced ready-to-use geopolymeric cement just like OPC for cementitious functions by adding water alone instead of hazardous alkaline solution
2. Advanced household cement-free green cements for manufacture of geopolymeric construction products like tiles, panels, and paver blocks addressing rural development
3. Advanced corrosion protection material to provide corrosion protection to mild steel.
4. Advanced geopolymeric instant repairing material to reconstruct or repair damaged structures

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